Self-Sustaining Cementitious Systems in Roman Reactive Glass Concretes

Marie D. Jackson, University of Utah

Team Members: Philip Brune, MNP LLC; Carol Jantzen; Philip Galland, Rob Hust, Silica Dynamics; Thomas Adams, KMR Collaborative; Bradley Cottle, Jacob Peterson, Jenny Hambleton, Pedro Romero, University of Utah

Project Goal

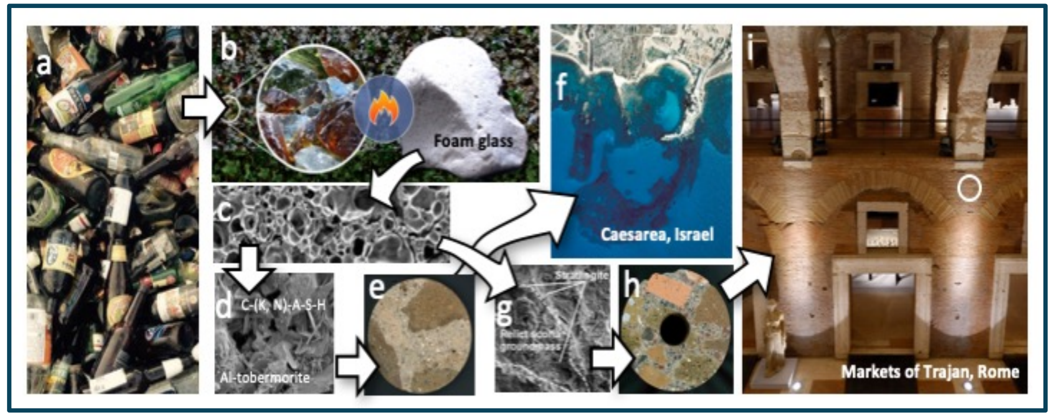
We are enhancing the reactivity of aggregates fabricated from recycled glass to produce pozzolanic and post-pozzolanic cementing phases in conglomeratic concretes that replicate the extremely durable and environmentally-friendly architectural and marine concrete systems of ancient Rome.

Total project cost:	$1.4 M
Current Q / Total Project Qs	Q9 / Q10

TINA-Cement
Annual Meeting
October 13 & 14, 2021

The Concept

- We utilize recycled waste glass and inexpensive additives to produce compositionally and texturally **Engineered Cellular Magmatics (ECMs)** to be used as reactive aggregates.
- The **ECM aggregates** mimic volcanic tephra that react pozzolanically and corrode beneficially to produce cementing phases in ancient Roman concretes.



Our innovative ECM materials, mortar mixtures and hydration technologies promote the self-sustaining cementitious systems of extremely durable Roman concretes that suppress fracture and create regenerative cementing systems at the millennial time scale. They improve durability at ~4 times typical 50-year OPCC service life; lower energy and emissions associated with production and deployment by ~85%; and keep costs competitive for a > 200 years service life.

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The Team

- **We are a multi-disciplinary team of scientists** from academia (University of Utah), industry partners (Silica Dynamics, MNP LLC, KMR Collaborative) and a national laboratory (Savannah River National Laboratories, Year 1)
- **Our core competencies** rest in glass science and fabrication of recycled glass derivatives, volcanic glasses and mineral cements, novel cementitious material design and testing, concrete fracture mechanics and Roman concrete materials and technologies.
- **Co-PIs and Subcontractors**

Carol Jantzen, Rob Hust, Philip Galland: Recycled glass ECM aggregate production, Geochemical modelling of reactive behavior

Philip Brune: Engineering fracture mechanics, testing and simulation, Roman concrete

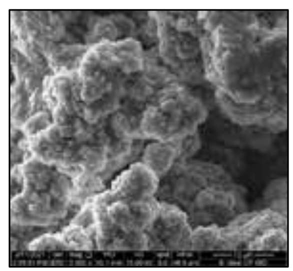
Thomas Adams: Civil engineering infrastructure and aggregates, Market dynamics

Marie Jackson: Volcanic glasses and tephras, Glass reactions and authigenic minerals, Roman concrete structures and mix design, Cementing binders and minerals

Project Objectives

- **YEAR 2**
- **Silica Dynamics**: Fabricated ECM compositional series that reproduce key attributes of targeted Roman volcanic tephras. Strong Base-Weak Acid models evaluate pozzolanicity and give mechanistic information about reactivity.
- **University of Utah**: Analyzed chemical, mineralogical and material characteristics of ECMs and associated cementitious materials.
- Developed a mortar pore fluid analysis and modelling technique to evaluate real-time lime-based pozzolanic activity.
- Developed an alkali-activated analytical and modelling technique to evaluate real-time post-pozzolanic activity.



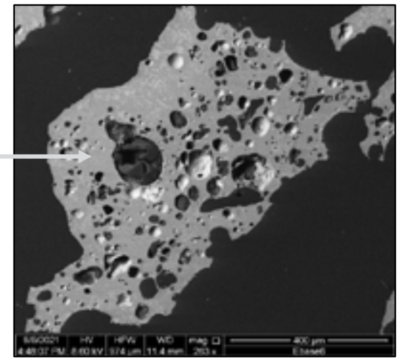
Project Objectives

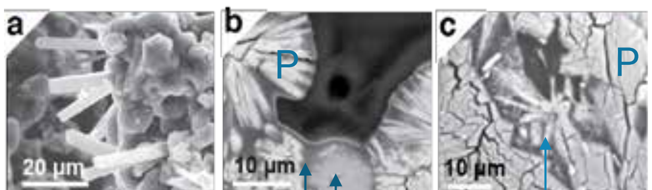
- **YEAR 2**
- **University of Utah-MNP LLC**: Implemented a novel indentation test to evaluate early age gains in stiffness in Roman marine mortar prototypes using ECMs (and a volcanic proxy).
- Implemented an arc-shaped bending test as a disruptive alternative to UCS tests.
- **Silica Dynamics-MNP LLC-KMR Collaborative**: Analyzed first markets for shoreline interface structures with extreme design life, low maintenance requirements and, potentially, regenerative repair of fracture surfaces

1) Importance of Alumina in ECM aggregates

- A successful ECM must mimic the 12–18 wt% Al_2O_3 in reactive tephra aggregates selected by Roman engineers.
- Our industry partner has recently achieved this ECM target.

Why is beneficially accessible alumina content critical to achieving the cost and performance attributes of our TEA?



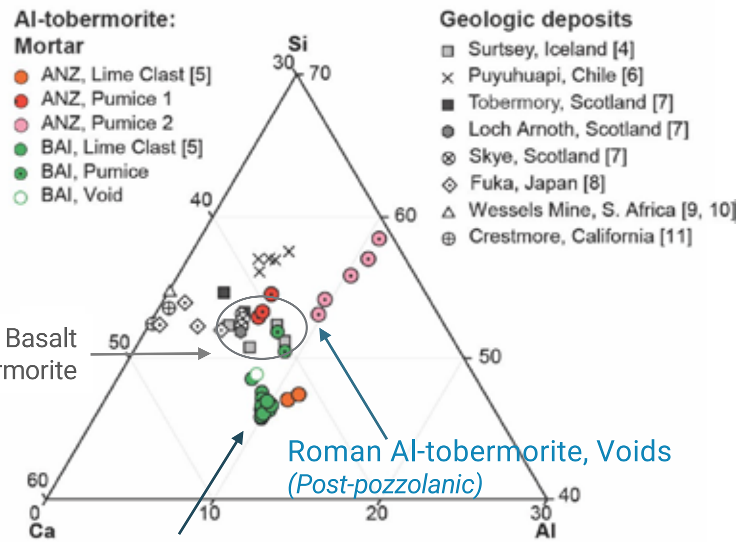


Surtsey basalt, Iceland

Pozzolanic C-A-S-H and Al-tobermorite

Post-pozzolanic Al-tobermorite

Surtsey Basalt Al-tobermorite



Roman Al-tobermorite, Voids
(Post-pozzolanic)

Roman Al-tobermorite, Relict lime clasts
(Pozzolanic)

Jackson et al. 2017, Phillipsite and Al-tobermorite mineral cements, *Am Mineralogist*,102, 1435–1450.

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Modeling C-A-S-H Phases in Roman Concretes with Geochemist's Work Bench (GWB) and CEM-ZEO Coupled Database

Carol Jantzen, GlassWRX

INFCA, INFCNA, 5CA, and 5CNA are acronyms that define 4 of 8 end members of the C-(N-)A-S-H gel structural sublattice solid solution model used for alkali activated slag (AAS) cements*
– the other 4 end members do not contain Al_2O_3

INFCA
$(CaO)_1(SiO_2)_{1.1875}(Al_2O_3)_{0.1562}(H_2O)_{1.66}$

Or can be written as
$CaSi_{1.1875}Al_{0.3124}O_{3.84} \bullet 1.66H_2O$

Al/(Si+Al) = 0.208

INFCNA
$(CaO)_1(SiO_2)_{1.1875}(Al_2O_3)_{0.1562}(Na_2O)_{0.34375}(H_2O)_{1.3125}$

Can be written as
$CaNa_{0.6875}Si_{1.1875}Al_{0.3124}O_{4.18375} \bullet 1.3125H_2O$

Al/(Si+Al) = 0.208

5CA
$(CaO)_{1.25}(SiO_2)_1(Al_2O_3)_{0.125}(H_2O)_{1.625}$

Or can be written as
$Ca_{1.25}Si_1Al_{0.25}O_4 \bullet 1.625H_2O$

Al/(Si+Al) = 0.20

5CNA
$(CaO)_{1.25}(SiO_2)_1(Al_2O_3)_{0.125}(Na_2O)_{0.25}(H_2O)_{1.375}$

Or can be written as
$Ca_{1.25}Si_1Al_{0.25}Na_{0.5}O_4 \bullet 1.375\ H_2O$

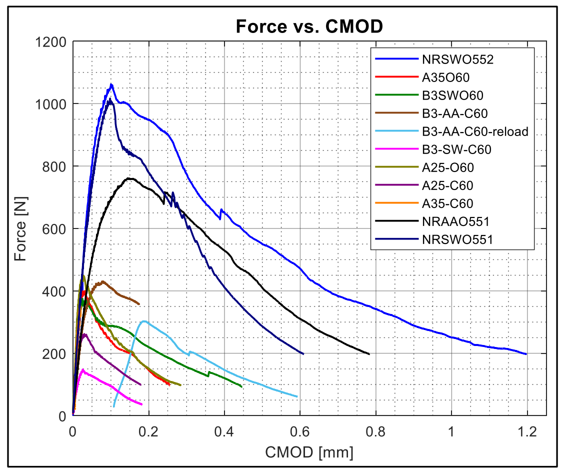
Al/(Si+Al) = 0.20

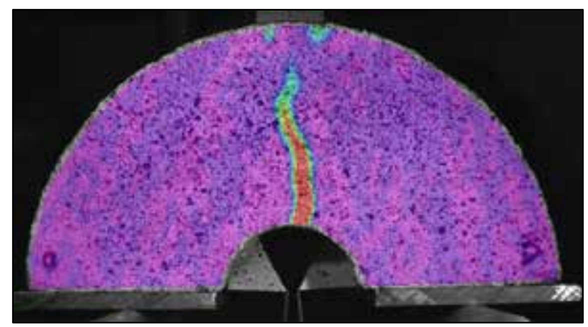
*Lothenbach, B., D.A. Kulik, T. Matschei, M. Balonis, L. Baquerizo, B. Dilnesa, G.D. Miron, and R.J. Myers, **"Cemdata18: A chemical thermodynamic database for hydrated Portland cements and alkali-activated materials,"** Cement and Con. Res. 115, 472-506 (2019).
Meyers, R.J., Bernal, S.A., and Provis, J.L., **"A Thermodynamic Model for C-(N-)A-S-H gel: CNASH_ss. Derivation and Validation,"** Cement and Con. Res., 66, 27-47 (2014).

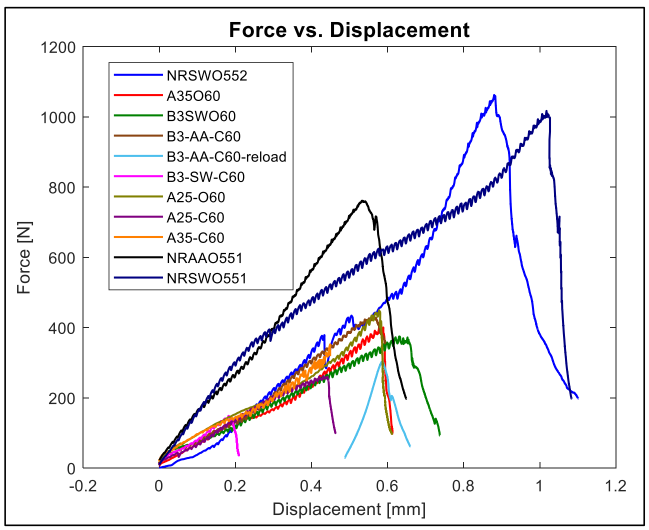
- **Major "unusual phases" in marine concretes are Al-tobemorite (CASH phase, phillipsite (a zeolite, $CaAl_2Si_6O_{16} \bullet 2.5H_2O$), some stratlingite ($Ca_2Al_2SiO_7(H_2O)_{5.5\text{-}8}$ and lime (CaO) clasts calcite/vaterite.**
  (Jackson et al. 2017 Am Min.)
- **Ratio of Al/(Al+Si) in Roman concretes important to formation of Al-Tobermorite**
  - **Al/(Al+Si) = 0.17-0.19**
    (Jackson et al. 2017 Am Min.)
- **Normal tobermorite (Taylor 1992)**
  $Ca_4(Si_{5.5}Al_{0.5}O_{17}H_2)]Ca_{0.2} \cdot Na_{0.1} \cdot 4H_2O$
  with Al/(Si+Al) = 0.08
- **Al-tobermorite usually forms from C_3A ($3CaO.Al_2O_3$) phase in Portland Cements (Suryavanshi et al. 1996) but there is no C_3A phase in Roman marine concretes.**

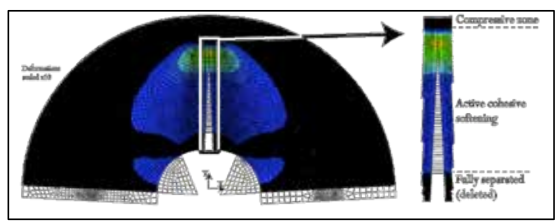
2) Arc Fracture Tests, ‘Ductility’, ‘Regenerative Repair’

- Post-fracture response is a key component of longevity for concrete structures, particularly in seawater environments
- Our arc-fracture test initiates and stably propagates a crack to quantify mechanical components of durability
- Our early-stage experimental materials show relatively high compliance and potential for ductility
- Subsequent testing will further quantify material performance and potential for ‘regenerative repair’









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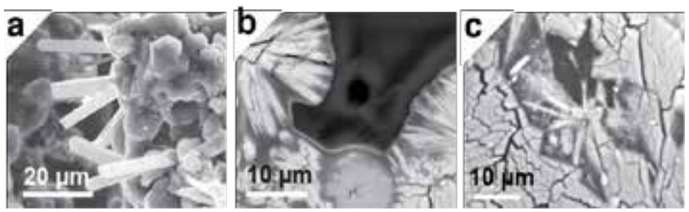
Challenges, Risks and Potential Partnerships

- *Biggest challenges – present and future ?*

  To implement transformative concepts in self-sustaining concrete technologies that emphasize chemical and mechanical resilience rather than compressive strength as measures of material performance and service life.

- *Success in reduction of present and future risk? How is our approach different?*



Jackson et al. 2017, *Am Mineralogist*

Roman marine concrete structures with 2000-year functional service lives provide precise compositional and technical targets that reduce risk in terms of 1) material development, 2) mix proportioning, 3) cementitious systems, and 4) preferred structural applications. Risks taken by Roman engineers strongly mitigate our risks.

ROMACONS DRILLING PROJECT 2002-2009

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Challenges, Risks and Potential Partnerships

- *Partnerships or other collaboration opportunities?*
  - Design-Build Contractors – Heavy Civil AE firms
  - Municipalities seeking innovative shoreline repair and interventions
  - Bureau of Reclamation
  - Army Corps of Engineers – Engineering with Nature Program

Any capabilities to offer other teams, or potential collaborations with other teams?

- Mineralogical and geochemical analysis of reactive cementitious components
- Dynamic modulus testing expertise

Technology-to-Market

- *Technology to commercialize:* High-performing material formulations and the manufacturing processes necessary to realize them.
- *Likely business model:* Technology licensing via commercial partners
- *Timeline to market*
  - Spring 2022: Scale Up demonstrations of functional shoreline structures
  - Fall-Winter 2022: Material assessments of functional shoreline structures
- *What is required to accelerate development and/or deployment of technology?*
  - Further laboratory verification of effective pozzolanic and post-pozzolanic reactions and cementing processes in candidate ECMs
- *Commercial applications and potential first markets, including first adopters*
  - Municipal marine infrastructure demonstration project on the East Coast: re-cycled and commonly available materials, ease of manufacture and placement, low embodied energy, anticipated century-scale design life , low life-cycle costs.
  - Innovative substrates for biomediated shoreline restoration projects.

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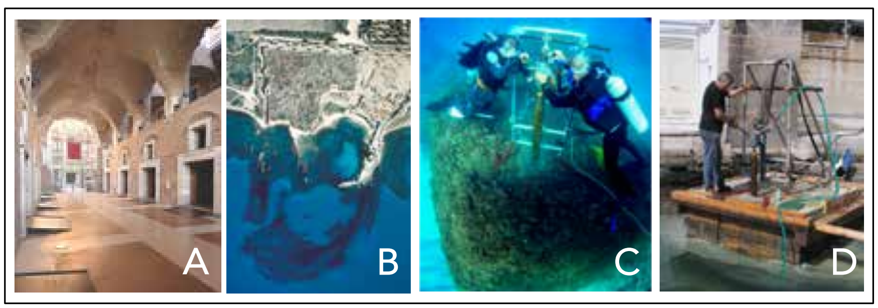
Summary - Roman Reactive Glass Concretes

- Advantages of Self-Sustaining Reactive Glass Concrete over OPC Concrete

SEA1 Estimated Material Performance Parameters		
Material Type	**OPCC**	**SEA1**
First Cost (per CY)	$155.00	$125.00
Design Life Span	35 Years	200 Years +
Material Cost (per CY)	$5.00/YR	$1.35
Reinforcing Steel (per CY)	$108.00	$0.00
Life Cycle Maintenance Cost	$15.00/CY	$10.00/CY
Life Cycle Cost	$5.50/CY/YR	$1.45/CY/YR
First Carbon Emission	0.28T/CY	0.23T/CY
Initial Cost to Install	**$935/CY**	**$62/CY**

Raw Materials.
Widely available waste glasses and carbonate rock.
Scalability.
Ubiquitous input materials - globally viable environmentally friendly marine concrete infrastructure.
Compatible with existing processes and techniques.
Works within existing construction materials production and distribution frameworks.
Cost competitiveness.
Estimated cost at parity with OPCC cost at $1.35 CY.
Time to Scale-Up production.
6 months.

- **March 2022** Completion of ARPA-E goals, milestones and deliverables



Insights from years of study are implemented in SEA1, a modern version of Roman marine concrete

U.S. DEPARTMENT OF ENERGY

https://arpa-e.energy.gov